4

MEASUREMENT OF DIELECTRIC PROPERTIES OF METAL SULPHIDES

M. N. SHARMA AND S. S. GUPTA

DEPARTMENT OF PHYSICS, LUCKNOW UNIVERSITY, LUCKNOW

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ABSTRACT Dielectric constants of some bivalent metal sulphides have been determined at radio frequency (7·25 Mc/s) using the method of mixtures. For ZnS, the force constant, K, has been evaluated and it compares well with other determinations. Compressibility, reststrahlen frequency, cohesive energy, ionic polarisation and Szigetis' short range correction factor 's', are subsequently calculated. The results are in good agreement with experimental values.

INTRODUCTION

Wiener (1910) has developed a formula taking into account the geometrical shape of the particles and their influence on the distribution of electric field, as the dielectric constant of crystalline powders depends also on the size and shape of the particles. Fricke (1924) has modified Wiener's formula and this modified formula has been used by us.

Compressibility and reststrahlen frequency of an ionic crystal are related to the dielectric constant and therefore they can be evaluated theoretically. Further, the force constant can also be evaluated with its help and if the law of interaction is known, interaction energy can also be computed. Dielectric constant data obtained experimentally for ZnS only has been treated for these properties, as the compressibilities and reststrahlen frequencies of other sulphides i.e. CaS, SrS and BaS are not known.

THEORY

Wiener's (1910) formula improved by Fricke (1924) for the case of spheroids immersed in a liquid medium, latter being continuous and homogeneous, is given as;

$$\frac{\epsilon_m-\epsilon_2}{\epsilon_m+u\epsilon_2} = v_1 \frac{\epsilon_1-\epsilon_2}{\epsilon_1+u\epsilon_2} \qquad \ldots (1)$$

where ϵ_m, ϵ_1 and ϵ_2 are the dielectric constants of the mixture and of the individual components, u is a factor depending on ϵ_1, ϵ_2 and the geometry of the particles, v_1 is the volume ratio of the components to that of the whole mixture.

Since at radio frequencies ϵ_1 and ϵ_2 are complex quantities, u is also complex, u being unknown, it is difficult to solve equation (1), for ϵ_1. Burton and Turnbulls'

method for solving equation (1) for ϵ_1 has been used earlier by Pradhan and Gupta (1959), and Sharma, *et al.* (1962). We have also used Burton and Turnbulls' method. This affords a simple and adequate approach for determining the dielectric constants of crystalline solids using the method of mixtures.

EXPERIMENTAL PROCEDURE

The mixtures of different sulphides were formed into experimental pastes in the following way :

The crystalline sulphides were powdered in a mortar and filtered through a fine mesh (1000 B.S.) This supplies almost similar sized particles which is our main requirement. The binding medium was taken to be liquid paraffin, which has ϵ 2.202 and negligible dielectric loss After efficient stirring homogeneous pastes having different known percentages of constituent sulphides were formed.

The dielectric constants of these pastes were determined by Hartshorns' method for the measurement of permittivity and power factor of dielectrics at radio frequencies, the method has been discussed in detail by Sharma (1960). Dielectric constants of mixtures thus measured are given in Table I.

The dielectric constants of metal sulphides were evaluated by the method described in preceding section, and are given in Table III, the constants used for obtaining these dielectric constants are given in Table II.

TABLE 1

Dielectric constants of mixtures

BaS		SrS		ZnS		CaS	
Conc. of salt %	ϵ_m	Conc. of salt %	ϵ_m	Conc. of salt %	ϵ_m	Conc. of salt %	ϵ_m
10 010	2.843	10.100	2.652	10.090	2 539	9.903	2 492
20.520	3.571	19.930	3.057	14 730	2 752	19.130	2.757
29.090	4 103	29.060	3.580	20.070	2.938	27.740	3 021
39.900	4.963	39 990	4 190	24 650	3.067	40.060	3.211
50 350	5.665	---	—	—	—	50.630	3 807

TABLE II

Values of '*u*' and '*x*' for metal sulphides

Crystal	BaS	SrS	ZnS	CaS
u	2 475	1 875	1.650	1.600
x	0.690	0.590	0.530	0.440

CORRELATION OF DIELECTRIC CONSTANT WITH OTHER PROPERTIES

The dielectric properties of ionic crystals are connected with the compressibilities, reststrahlen frequencies and interaction energies.

The potential energy $E(r)$ of the crystal per pair of ions can be written as :

$$E(r) = -\frac{\alpha e^2 Z^2}{r} + \phi(r) \qquad \ldots \quad (2)$$

where, α, is the Madelung constant r is the inter-ionic distance and Z is the ionic valency of the crystal. $\phi(r)$ contains all the rest of the energy which is not contained in the electrostatic term. Various forms of $\phi(r)$ have been suggested but we have taken the simplest form of $\phi(r)$ i.e.

$$\phi(r) = \frac{B}{r^n} \qquad \ldots \quad (3)$$

where B is a repulsive force parameter and n is a Born constant. Eq.(3) does not take into account the van der Waals forces as the required data of these force parameters are not known. Hence equation (2) takes the form

$$E(r) = -\frac{\alpha e^2 Z^2}{r} + \frac{B}{r^n} \qquad \ldots \quad (4)$$

The force constants a_1, used by Krishnan and Roy (1951) and K used by Born and Huang (1954) are given by

$$K = 2a_1 \qquad \ldots \quad (5)$$

where

$$K = \frac{1}{3}\left[\frac{2\phi'(r)}{r} + \phi''(r)\right] \qquad \ldots \quad (6)$$

in which $\phi'(r)$ and $\phi''(r)$ are the first and second derivative of the overlap potential between a positive and negative ion.

If we consider a uniformly polarized sphere in the absence of an external electric field, the only forces acting are due to $\phi(r)$ term as shown by Szigeti (1951), the Lorentz effective field F being equal to zero, and we can write a relation connecting K and β, (the compressibility) as,

$$K = \frac{3u}{\beta r^2} \qquad \ldots \quad (7)$$

where u is the volume occupied by an ion pair. The force constant K, when $F = 0$, is connected with the reststrahlen frequency ω_0 as

$$K = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} m\omega_0^2 \qquad \ldots \quad (8)$$

where ϵ_0 and ϵ_∞ are the static and high frequency dielectric constants and m is the reduced mass. Krishnan and Roy (1951) treat this problem in a slightly different way. As a result of lattice displacement, there is a development of a homogeneous electric polarization in the crystal and the value of the force coefficient K, instead of being only due to the $\phi(r)$ term will be less by an amount proportional to the force due to the polarization field.

From the polarization, the contribution to the force coefficient will be

$$2a_2 = -\frac{4}{3}\pi Ne^2 \qquad \ldots \quad (9)$$

and the total force coefficient then becomes

$$2a = 2a_1 + 2a_2 = m\omega_0^2 \qquad \ldots \quad (10)$$

Therefore,

$$K = m\omega_0^2 - 2a_2 = 2a_1 \qquad \ldots \quad (11)$$

Utilizing the experimentally determined values of the dielectric constant ϵ_0, we can evaluate the value of the force coefficient K, provided we know the reststrahlen frequency ω_0. This in turn will enable a determination of the interaction energy of the undeformed crystal as well as its compressibility. The values of β and K (from 11 and 8) are given in Tables V and VI respectively, where they have been compared with other determinations. Recently, compressibility data is available only for ZnS and hence one could also take the experimental value of β and use it to calculate K. This can then give the reststrahlen frequency using either equation (8) or (11). The value of ω_0 thus computed is given in Table VI. Using experimental ω_0 and experimental β, theoretical value of dielectric constant can also be computed for ZnS crystal this value of dielectric constant is given in Table VI, where it has been compared with experimental value.

The expression for interaction energy is given by the relation

$$U(r) = \frac{3r^2}{n(n-1)}\left[K - \frac{n(n-1)}{3r^2}\frac{\alpha e^2}{r}\right] \qquad \ldots \quad (12)$$

where $n = 9$ for ZnS. The value of interaction energy using equation (12) is given in Table V.

RESULTS AND DISCUSSION

The dielectric constants of metal sulphides given in Table III show that the dielectric constant is maximum for BaS and minimum for CaS, i.e., it increases as the molecular weight of the ionic crystal decreases and vice versa. This behavior

can be explained if we consider the ionic polarization of these crystals. The dielectric constant of a material can be attributed to polarizability and may be due to electronic, ionic or orientation factors. The electronic contribution arises from the displacement of electrons in an atom relative to the nucleus, i.e., from the deformation of the electronic shell about the nucleus. The ionic or atomic contribution is due to the displacement of a charged ion with respect to the other ions. If the substance is built up of molecules possessing permanent electric dipole moments the orientation or dipolar polarization occurs. In the case of ordinary ionic crystals there is no dipolar contribution, and ionic contribution is seldom larger than the electronic contribution.

The ionic and electronic contributions can be separated from the following relation;

$$\Delta\epsilon = (\epsilon_0 - n^2) \qquad \ldots \quad (13)$$

where ϵ_0, the dielectric constant of the crystal, arises almost entirely from the electronic polarizability, n is the refractive index of crystal in the optical range (in the electrical frequency range, the dielectric constant arises from both ionic and electronic polarizabilities), and $\Delta\epsilon$ is the contribution due to ionic polarizability. The value of $\Delta\epsilon$ for ZnS is given in Table IV along with the value of n.

The magnitude of the electronic polarization is given by Szigeti (1949) as,

$$(\epsilon - n^2) = \left(\frac{n^2+2}{3} \right)^2 4\pi n \, \frac{(SZe)^2}{m\omega_t^2} \qquad \ldots \quad (14)$$

where ϵ is the static dielectric constant, n the optical refractive index, ω_t the infra-red absorption frequency and m, the reduced mass of an ion pair defined by,

$$\frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \ldots \quad (15)$$

m_1 and m_2 being the masses of the two atoms. Z is the valency of the ions and e the electronic charge, S is defined by,

$$\mu_s(x) = SZex \qquad \ldots \quad (16)$$

where μ_s is the dipole moment per ion pair in a spontaneously polarized sphere, if x is the displacement of the two kinds of ions relative to each other. As the effective field vanishes in the Lorentz approximation, there should be no elec-

TABLE III

Dielectric constants of metal sulphides

Crystal	Structure	Present	Born and Huang (1954)
BaS	NaCl	19.230	
SrS	NaCl	11 310	—
ZnS	Zinc-blende	8.780	8 300
CaS	NaCl	6.699	—

TABLE IV

Comparison of 'S' values for ZnS

ε	n^2	$\Delta\varepsilon$	S Values Present	S Values Szigeti (1951)
8.78	5 07	3 71	0.516	0 480

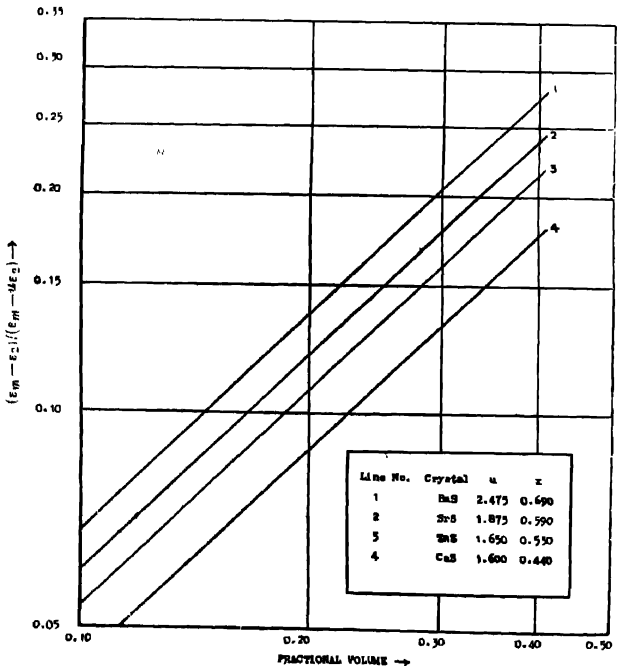

Fig. 1. Interpolation for obtaining 'X' values for different sulphides.

TABLE V

Values of compressibility and cohesive energy for ZnS

Compressibility ($\beta \times 10^{-12}$ cm./dyne)				Cohesive energy in K. cals /mole				
Experimental	From equ. (11) and $\omega_{0(expt.)}$	From equs. (11) and (14)	equ. (7)	Observed	Using K from equ (8)	K from equ (7) $\beta_{(expt.)}$	K from equ. (11)	K from equ. (14)
1 280	1.331	1 185	1 237	851.0	876 4	878 8	880 8	875 6

TABLE VI

Values of reststrahlen frequency, force constant and dielectric constant

Reststrahlen frquency $\times 10^{-13}$				Force constant $\times 10^{-4}$				Dielectric constant	
Observed	From equ. (14) and $\varepsilon_{(expt}$	Using $\beta_{(expt.)}$ and equ. (8)	Using $\beta_{(expt.)}$ equ. (11)	From equ. (11)	From equ. (8)	From equ (7) and $\beta_{(expt.)}$	From equ. (14)	Observed	Calculated
5.710	6.187	5.617	5 866	16.49	17 74	17 15	18.53	8.78	8 42

tronic polarization in this case, and μ_s ought to be equal to zero. In other words, in Lorentz approximation S would be unity

Eq (8) holds better than equation (14), particularly for alkali halides as shown by Hardy (1960), who has given a detailed discussion of the importance of relations (8) and (14). The effect of equation (14) can be seen if one uses this relation and the experimental c_0 to calculate the compressibility which can be compared with the values given in Table V based on equation (8). The calculated value of S for ZnS employing equation (14) is given in Table IV along with Szigetis' value. A fair agreement is observed The author's value is slightly higher than Szigetis value showing that there is less overlap or short range interaction in the radio frequency region.

Comparison of various values in Tables V and VI shows that there is a reasonable agreement between themselves and also with the experimentally determined values.

A comparison of reststrahlen frequency indicates that the value of ω_0 calculated by using experimental β is in better agreement with the observed frequency, thus placing confidence in the experimental value of β.

Table V shows that the calculated value of β is smaller than experimental β. This is due to the fact that as a result of increasing electron sharing the distortions caused by the neighbouring ions are no longer sufficiently localised to be independent of each other.

In view of the fact that ZnS is less ionic than alkali halides studied earlier by Sharma, *et al.* (1962), much importance is to be attached to the remarkable agreement in the case of ZnS for various properties. It has been mentioned by Szigeti (1951) that the experimental data for some of the crystals, which are not alkali halides, may contain fairly large errors, and this may be the case for ZnS.

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